Statistical Thermodynamics in Chemistry and Biology

3. Heat, work and energy

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January 18, 2016

Conservation laws

Some properties are conserved:

- Linear momentum (but not velocity)

$$\sum_i \vec{p}_i = \sum_i m_i \vec{v}_i$$

- Mass
- Energy (but not heat)
- Not mentioned here: charge is also conserved. Electroneutrality is actually a very strong macroscopic condition.
- A property that is conserved can only flow from one place to another.

Force and work

Force

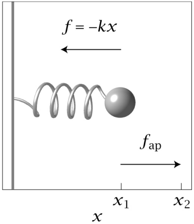
Newton's second law defines the force in terms of acceleration as

$$\vec{F} = m\vec{a} = m\frac{d^2\vec{r}}{dt^2}$$

Work: ball on a spring

- Intrinsic force, $f = -kx$, from the spring
- Applied force, $f_{\mathrm{ap}} = -f$
- The work, dw, on the system by moving the ball towards right a distance, dx,

$$dw = f_{\mathrm{ap}} dx = -f dx$$



- The total work is given as

$$w = \int_{x_1}^{x_2} dw = \int_{x_1}^{x_2} f_{\mathrm{ap}} dx = -\int_{x_1}^{x_2} f dx = k\int_{x_1}^{x_2} x dx = \frac{k}{2}\left(x_2^2 - x_1^2\right)$$

Energy

Kinetic energy

The kinetic energy, K, of a particle with a mass, m and a velocity, $\vec{v}$ is given as

$$K = \frac{1}{2} m \vec{v} \cdot \vec{v} = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right) = \frac{1}{2} m v^2$$

Potential energy

The potential energy, V, is given by the position only; it is the work an object can perform by virtue of its position. Coulomb's law is an example:

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 R_{12}}$$

Total energy

The total energy, E, is conserved:

$$E = K + V$$

The first law of thermodynamics

The internal energy, U, which is the sum of heat, q, and work, w, is conserved:

$$U = q + w$$

- Heat and work can be interconverted
- Work can be of various forms: mechanical, electrical, magnetic, etc.
- Heat radiation: electromagnetic radiation and heat can be interconverted: Planck's law:

$$\Delta E = h\nu = \hbar\omega$$

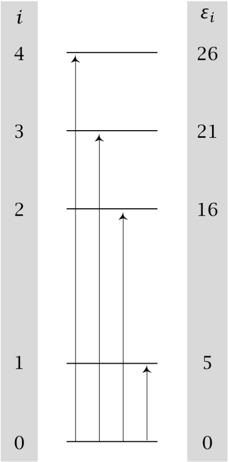
Atoms and molecules have quantized energies

- For a system of non-interacting particles (such as an ideal gas), the total microscopic energy, E,

$$E = \sum_{i=0}^{\infty} n_i \varepsilon_i$$

- The (average of the) microscopic energy, E, is the same as the internal energy, U.
- If U is increased by heating, the energy levels do not change. The population, n_i, change.
- In contrast, work changes the energy levels, ε_i, not the populations.
- Consider a change of the energy, dE,

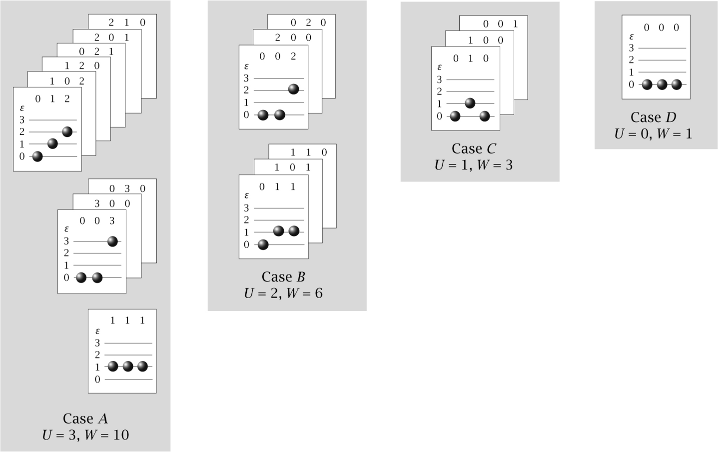
$$dE = \sum_{i=0}^{\infty} (dn_i \varepsilon_i + n_i d\varepsilon_i) = dq + dw = dU$$



Why does heat flow?

- We have previously demonstrated that a gas expands because the multiplicity, $W(V)$, increases with the volume, V. That defines pressure.
- We have also demonstrated that particles mix because the multiplicity, $W(N)$, increases as particle segregation decreases. That defines chemical potential.
- These are manifestations of the principle that systems tend to their state of maximum multiplicity.
- We will now investigate the flow of heat from hot to cold.

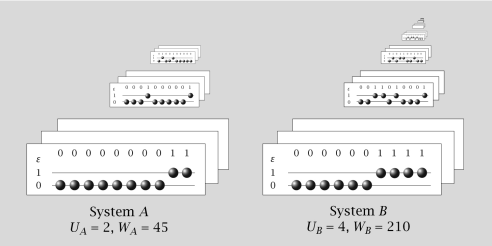
How does multiplicity depend on energy?



- Miniaturized model of a material: three particles.
- i=0, 1, 2,. . ., energy levels with energy, $\varepsilon_i = i$
- $W(U)$ is an increasing function with U.

Why does energy exchange?

- Two systems, A and B. Each system has 10 particles and 2 energy levels, $\varepsilon_0 = 0$ and $\varepsilon_1 = 1$.



- Given internal energies for each subsystem, U_A and U_B, the multiplicity W: $W(U_A, U_B) = W_A(U_A) \times W_B(U_B)$

$$\text{Start system:} \qquad W(2,4) = \frac{10!}{2!8!} \times \frac{10!}{4!6!} = 45 \times 210 = 9450$$

$$\text{End system:} \qquad W(3,3) = \frac{10!}{3!7!} \times \frac{10!}{3!7!} = 120 \times 120 = 14400$$

- How does the heat flow? Do we do any work on the system?

Energy can flow uphill

- Same system, but now consider a system with unequal amount of particles in A and B.
- Case 1: $N_A = 10$, $N_B = 4$, $U_A = 2$, $U_B = 2$
- The multiplicity becomes

$$W = W_A \times W_B = \frac{10!}{2!8!} \times \frac{4!}{2!2!} = 45 \times 6 = 270$$

- Case 2: $N_A = 10$, $N_B = 4$, $U_A = 3$, $U_B = 1$. What happens?
- The multiplicity becomes

$$W = W_A \times W_B = \frac{10!}{3!7!} \times \frac{4!}{1!3!} = 120 \times 4 = 480$$

- Energy is not equalized.
- We will demonstrate shortly that heat flows so that temperature is equalized.

Second law of thermodynamics

- The principle of maximum multiplicity is the second law of thermodynamics.

Summary

- Energy:
  - In classical mechanics, the energy is divided into a kinetic energy and a potential energy.
  - In quantum mechanics, the particles populate energy levels.
  - In thermodynamics, the internal energy, U, is divided into work and heat.
- Microscopic interpretation of heat and work:
  - Heating changes the population of the energy levels in a quantum mechanical system.
  - Work changes the energies of the quantum mechanical states, not the populations of the states.
- Connection between the microscopic and macroscopic worlds: The microscopic total energy, E, is regarded as the internal energy, U, in thermodynamics.
- The flow of heat from a hot body to a cold body can be explained by the principle of maximizing the multiplicity.
- The principle of maximum multiplicity is the second law of thermodynamics.